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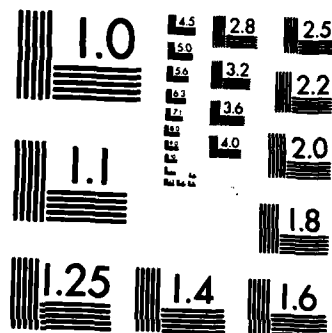
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GAS-LIQUID CORRELATION OF IONIZATION ENERGIES

by

Paul Delahay and Andrew Dziedzic

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GAS-LIQUID CORRELATION OF IONIZATION ENERGIES

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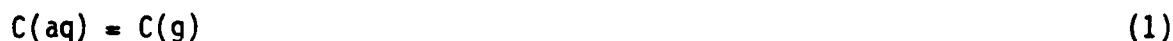
Ionization potentials of ions and molecules are correlated with the threshold energies of their aqueous solutions for photoelectron emission. Inner- and outer-sphere reorganizations are treated, respectively, in terms of a discrete number of dipoles and a continuous medium model. Calculated and experimental threshold energies are compared for halide and hydroxide ions and water. The threshold and reorganization energies of the hydrated electron are calculated from threshold energies of anions and their absorption spectra for charge transfer to the solvent.

1. Introduction

The threshold energies for photoelectron emission by aqueous solutions will be correlated (i) with gas-phase ionization energies and electron affinities, and (ii) with absorption spectra for charge transfer to the solvent. The first correlation will be established on the basis of a recent treatment [1] of the free energy for inner-sphere reorganization in the photoionization of univalent anions and molecules. Ionization energies of clusters of water molecules in the gas phase obtained in recent [2] ab initio SCF MO calculations will be used to estimate the liquid-phase ionization energy of liquid water. The second correlation will be applied to the calculation of the threshold energy of the hydrated electron.

2. Free energy of emission and gas-phase ionization

Consider the photoelectron emission by an aqueous solution of a substance C. The change of free energy from initial to final state for the emission process is obtained from the sequence,



where (aq) and (g) denote respectively the liquid and gas phases. The change of free energies for (1) to (3) are, respectively, $-\Delta G_S(C)$, ΔG_i and $\Delta G_S(C^+)$, where the ΔG_S 's pertain to hydration and ΔG_i to ionization ($\Delta G_i \approx I$, the ionization potential).

The free energy of emission ΔG_m is obtained by including the total free energy of reorganization [3] and a term for the surface potential in the summation of free energies. Thus,

$$\Delta G_m = I + \Delta G_S(C^+) - \Delta G_S(C) + R_{in} + R_{out} + |e|x, \quad (4)$$

where the positive quantities R_{in} and R_{out} are respectively the inner- and outer-sphere reorganization free energies; e is the electronic charge and the surface potential of the solution ($|ex| < 0.1$ eV in general [4]). Equation (4) will be applied to anions (sec. 3) and water (sec. 4).

3. Anions

Explicit forms of R_{in} and R_{out} will be introduced in eq. (4) for emission by aqueous solutions of univalent anions $A^-(aq)$. Thus [1],

$$R_{in} = - [\Delta G_S(A^-) - \Delta G_B - U(ep_\alpha) - U(p_\alpha p_\alpha) - U_{IND} + \Delta G_S(A)], \quad (5)$$

where ΔG_B is the free energy for Born charging of the dielectric (solvent) in the outer-sphere region; $U(ep_\alpha)$ and $U(p_\alpha p_\alpha)$ the energies for charge-induced dipole and induced dipole-induced dipole interaction; U_{IND} the energy for induced dipole formation in the inner-sphere solvation shell.

Equation (5) is obtained [1] by noting that photoelectron emission by $A^-(aq)$ is the opposite process of hydration of $A^-(g)$ except that the negative charge is removed by electrons in emission and the hydrated atom or radical $A(aq)$ is left in solution. The term ΔG_B and the U 's are subtracted from $\Delta G_S(A^-)$



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in eq. (5) since Born charging is taken into account by the term R_{out} and interaction with induced dipoles does not involve a change in nuclear coordinates. A minor contribution from London dispersion considered in [1] is omitted in (5). Negligible quadrupole-induced dipole interaction is also omitted.

The term ΔG_B in eq. (5) will be combined with the term R_{out} appearing in eq. (4). Thus,

$$\Delta G_B = - (1 - \epsilon_s^{-1})e^2/2a, \quad (6)$$

where ϵ_s is the static dielectric constant of water, and $a = r_c + 2r_w$, r_c and r_w being, respectively, the crystallographic radii of $A^-(g)$ and water ($= 1.38 \text{ \AA}$). Conversely,

$$R_{out} = (\epsilon_{op}^{-1} - \epsilon_s^{-1})e^2/2a, \quad (7)$$

where ϵ_{op} ($= 1.777$ at 25°C) is the limiting value of the optical dielectric constant of liquid water in the visible range.

One obtains from (4) to (7) after setting I equal to the electron affinity A_e of $A(g)$,

$$\Delta G_m = A_e - 2\Delta G_S(A^-) + P_{out}^e + U(ep_\alpha) + U(p_\alpha p_\alpha) + U_{IND} + |e|x, \quad (8)$$

with

$$P_{out}^e = - (1 - \epsilon_{op}^{-1})e^2/2a. \quad (9)$$

The quantity P_{out}^e is the free energy of electronic polarization of the dielectric (solvent) for the outer-sphere region for a continuous medium model. Conversely, the U 's in eq. (8) pertain to a discrete number of induced dipoles in the inner-sphere region. One has [5],

$$U(ep_\alpha) = - N e p_\alpha / (r_c + r_w)^2 \quad (10)$$

$$U(p_\alpha p_\alpha) = b p_\alpha^2 / (r_c + r_w)^3 \quad (11)$$

$$U_{IND} = (1/2\alpha) N p_\alpha^2, \quad (12)$$

where N is the number of water molecules in the inner-sphere hydration shell of

$A^-(aq)$; p_α the induced dipole of the solvent; b a structure constant depending on N (2.296 and 7.114 for $N = 4$ and 6 , respectively); α ($= 1.444 \times 10^{-24} \text{ cm}^3$) the polarizability of the water molecule. The induced dipole p_α is calculated most simply from

$$p_\alpha = \alpha e / (r_c + r_w)^2. \quad (13)$$

Values of ΔG_m from eq. (8) are listed in Table I (data from [6] to [9]) and are compared with the experimental threshold energies E_t . The surface potential was taken to be that of water ($0.08 \pm 0.06 \text{ eV}$ [4]). The contribution from vibrational relaxation to R_{in} for OH^- is negligible since the interatomic distance O-H is the same within 0.002 \AA for $\text{OH}^-(g)$ and $\text{OH}(g)$ [8]. Agreement is as good as one could expect in view of some uncertainty about hydration free energies (cf. [6] vs. [9]).

Structure in the hydration shell can be taken into account on the basis of the treatment of hydration in [5]. Thus, the radius $a = r_c + 2r_w = r_c + 2.76 \text{ \AA}$ in eq. (9) is set equal to $r_c + 2.19 \text{ \AA}$ and $r_c + 2.51 \text{ \AA}$ for $N = 4$ and 6 , respectively. The induced dipole p_α is obtained in [5] by minimizing the total free energy of the processes involving induced dipoles in hydration (cf. eq. (25) in [5]). The resulting values of P_{out}^e , the sum of the U 's of (10) to (12) and ΔG_m are listed in the second row for each ion in Table 1. The results are similar to those of row I.

The term P_{out}^e in eq. (8) follows from a continuous medium model whereas the U 's of (10) to (12) are calculated for a discrete number of induced dipoles. One may try to replace the sum of P_{out}^e and the U 's in eq. (8) by a single quantity P^e calculated for a continuous medium outside the spherical cavity of radius r_c , namely

$$P^e = - (1 - \epsilon_{op}^{-1}) e^2 / 2r_c. \quad (14)$$

The values of ΔG_m computed in this way are listed in Table 1, third row for each ion. These results are, of course, approximate.

4. Water

Equation (4) is readily transposed to photoelectron emission by liquid water. Process (1) involves the free energy of vaporization ΔG_{vap} ($= 0.09$ eV) of water, and eq. (4) becomes

$$\Delta G_m = I + \Delta G_S(\text{H}_2\text{O}^+) + \Delta G_{\text{vap}} + R_{\text{in}} + R_{\text{out}} + |e|x_{\text{H}_2\text{O}}, \quad (15)$$

where $x_{\text{H}_2\text{O}}$ ($= 0.08 \pm 0.06$ eV [4]) is the surface potential of water. Equation (5) for R_{in} now becomes

$$R_{\text{in}} = - [\Delta G_S(\text{H}_2\text{O}^+) - \Delta G_B - U(ep_\alpha) - U(p_\alpha p_\alpha) - U_{\text{IND}} - \Delta G_{\text{vap}}], \quad (16)$$

where $\Delta G_{\text{vap}} = -\Delta G_S(\text{H}_2\text{O})$. The final result,

$$\Delta G_m = I + 2\Delta G_{\text{vap}} + P_{\text{out}}^e + U(ep_\alpha) + U(p_\alpha p_\alpha) + U_{\text{IND}} + |e|x_{\text{H}_2\text{O}}, \quad (17)$$

is similar to eq. (8), but the term $-2\Delta G_S(A^-)$ for hydration of $A^-(g)$ in the latter is now replaced by $2\Delta G_{\text{vap}}$ for vaporization. Vibrational relaxation is negligible since the vertical and adiabatic gas-phase ionization energies are practically the same.

Assuming that the crystallographic radius r_c of H_2O^+ is the same as $r_w = 1.38$ Å for water, one computes $P_{\text{out}}^e = -0.76$ eV from (9), $p_\alpha = 0.91$ debye from (13), $U(ep_\alpha) = -1.43$ eV from (10) for $N = 4$, $U(p_\alpha p_\alpha) = 0.06$ eV from (11), $U_{\text{IND}} = 0.72$ eV from (12). Equation (15) yields $\Delta G_m = 11.47$ eV for $I = 12.62$ eV, $\Delta G_{\text{vap}} = 0.09$ eV and $|e|x_{\text{H}_2\text{O}} = 0.08$ eV whereas the experimental threshold energy is 10.04 ± 0.02 eV. Applying the method of [5] as in sec. 3, one computes $P_{\text{out}}^e = -0.88$ eV, $U(ep_\alpha) = -1.17$ eV, $U(p_\alpha p_\alpha) = 0.04$ eV, $U_{\text{IND}} = 0.46$ eV, $\Delta G_m = 11.31$ eV. This value of ΔG_m is still too high by ca. 1.3 eV in comparison with the experimental threshold, and the calculation of ΔG_m is definitely less satisfactory for water than for the ions in sec. 3. The preceding calculation of ΔG_m of water is inadequate for the following reasons: (i) Most importantly, the model with spherical symmetry implied by the equation used in the calculation of ΔG_m only provides a crude approximation for a species such

as H_2O^+ even with the improvement of [5]. (ii) The number $N = 4$ of nearest neighbors holds for ice but is higher for liquid water, namely $N \approx 4.4$ on the average near 0°C [10]. (iii) Hydrogen bonding was not considered in the derivation [1] of eq. (5) for R_{in} .

Just as was done in sec. 3, one can replace the sum of P_{out}^e and the sum of the U 's in eq. (15) by the free energy P^e of eq. (14). One computes $P^e = -2.28$ eV and $\Delta G_m = 10.6$ eV. This result is to be compared with $E_t = 10.04 \pm 0.02$ eV, but the treatment is very approximate. The equation for ΔG_m with the term P^e is identical to the equation in [11,12] for photoionization in the bulk of a condensed phase (except for the non-applicable term $2\Delta G_{\text{vap}}$ and the contribution from the conduction band level in the liquid in [12]).

The results of recent SCF MO calculations of the ionization energies of clusters of water molecules in the vapor phase [2] can be used to estimate the sum $U(ep_\alpha) + U(p_\alpha p_\alpha) + U_{\text{IND}}$ in eq. (17). Consider clusters consisting of a water molecule undergoing photoionization which is surrounded by 1 to 4 water molecules. The ionization energy of these clusters is lowered by 1 to 4 times the sum of the following energies: interaction between the ion H_2O^+ and the surrounding induced dipoles, induced dipole-induced dipole interaction, and formation of induced dipoles to a first approximation. This sum (in eV) per induced dipole is accordingly $(12.62 - I_n)/(n - 1)$ (Table 2), that is, 0.35 eV. Hence, one has in eq. (17), $U(ep_\alpha) + U(p_\alpha p_\alpha) + U_{\text{IND}} = -4 \times 0.35 = -1.4$ eV approximately. This energy is twice the result (-0.71 eV) obtained from eqs. (10) to (13). Neglecting hydrogen bonding as before, one obtains from eq. (17) $\Delta G_m \approx 10.6$ eV (for $P_{\text{out}}^e \approx -0.9$ eV and $|e|x_{\text{H}_2\text{O}} = 0.08$ eV). This calculation is quite crude, but it yields a result closer to the experimental threshold energy (10.04 ± 0.02 eV) than eqs. (10) to (13) and the method of [5]. The ionization energy of the cluster for $n = 2$, $12.62 - 0.35 \approx 12.3$ eV, calculated from this simple model is fairly close to the recently determined experimental value of 12.1 ± 0.1 eV [13].

5. Hydrated electron

The free energy of emission of the hydrated electron is obtained by transposition of the cycle (1) to (3) in sec. 2. Thus,

$$\Delta G_m = -\Delta G_s(e^-) + R + |e|_{\chi_{H_2O}}, \quad (18)$$

where $\Delta G_s = -1.62$ eV [14] is the free energy of hydration of the electron and R is the reorganization free energy of the cavity in the liquid left upon removal of the electron. The quantity R will be computed from the correlation between threshold energies of anions and their absorption spectra for charge transfer to the solvent. The following relationship is derived in [15]:

$$\Delta G_m - \Delta G_H = \Delta G_{CT} - \Delta G - R + R(D^-A), \quad (19)$$

where ΔG_m is the free energy of emission for the donor (anion) D^- ; $\Delta G_H = 4.48$ eV is the free energy for $1/2H_2(g) = H^+(aq) + e^-(g)$; ΔG_{CT} is the free energy for the charge transfer process $D^-A \rightarrow DA^-$; $\Delta G = 2.77$ eV [14] is the change of free energy for $1/2H_2(g) = H^+(aq) + e^-(aq)$; and

$$R(D^-A) = (\epsilon_{op}^{-1} - \epsilon_s^{-1})e^2/r_{D^-A}, \quad (20)$$

with

$$r_{D^-A} = r_c + 2r_w + r_v, \quad (21)$$

where r_c and r_w are the crystallographic radii of the anion and water, respectively, and $r_v = 0.91$ Å [16] is the radius of the void in water associated with the hydrated electron.

One sets $\Delta G_m = E_t$ in eq. (19) for the donor anion and $\Delta G_{CT} = E_{max}$ at the maximum of the charge transfer absorption band [17]. Thus,

$$R = E_{max} - E_t + \Delta G_H - \Delta G + R(D^-A), \quad (22)$$

where $\Delta G_H - \Delta G = 4.48 - 2.77 = 1.71$ eV is the free energy for the process $e^-(aq) = e^-(g)$. This free energy is also equal to $-\Delta G_s(e^-) + |e|_{\chi_{H_2O}} = 1.62 + 0.08 = 1.70$ eV, where the uncertainty on the surface potential is ± 0.06 eV. The values of $\Delta G_H - \Delta G$ and $-\Delta G_s(e^-) + |e|_{\chi_{H_2O}}$ therefore are self-consistent.

Possible contribution from the vibrational relaxation energy of the radical produced by photoionization is neglected in eq. (22).

Values of R computed from (20) to (22) and listed in Table 3 yield a mean value of $R = 1.25$ eV (0.10 eV standard deviation) in reasonable agreement with the energy of 1.48 eV from model calculations [16]. The corresponding free energy of emission of the hydrated electron from (18) is $1.62 + 1.25 + 0.08 = 2.95$ eV (0.13 eV standard deviation).

The values of $R(D^-A)$ and R in Table 3 are not very different for each anion except ferrocyanide, and consequently one has $E_t - \Delta G_H = E_{\max} - \Delta G$ to a first approximation [15]. Ferrocyanide ion is exceptional because its size causes $R(D^-A)$ to be unusually low (0.97 eV).

Acknowledgment

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Table 1

Calculated emission free energies of anions vs. experimental threshold energies^{a)}

| | $r_c^{b)}$ (Å) | $A_e^{c)}$ (eV) | $-\Delta G_S(A^-)^{d)}$ (eV) | $-p_{out}^e$ (eV) | U^e (eV) | p^e (eV) | $\Delta G_m^f)$ (eV) | E_t (eV) |
|-----------------|-------------------|--------------------|---------------------------------|----------------------|---------------|---------------|-------------------------|---------------|
| Cl ⁻ | 1.81 | 3.61 | 3.30 | 0.69 | -0.55 | - | 9.05 (I) | 9.0 |
| | | | | 0.73 | -0.51 | - | 9.05 (II) | |
| | | | | | | -1.74 | 8.5 (III) | |
| Br ⁻ | 1.95 | 3.36 | 3.14 | 0.67 | -0.49 | - | 8.56 (I) | 8.2 |
| | | | | 0.71 | -0.43 | - | 8.58 (II) | |
| | | | | | | -1.61 | 8.1 (III) | |
| I ⁻ | 2.16 | 3.06 | 2.66 | 0.64 | -0.37 | - | 7.45 (I) | 7.4 |
| | | | | 0.67 | -0.34 | - | 7.45 (II) | |
| | | | | | | -1.46 | 7.0 (III) | |
| OH ⁻ | 1.47 | 1.83 | 3.93 | 0.74 | -0.59 | - | 8.44 (I) | 8.6 |
| | | | | 0.86 | -0.59 | - | 8.32 (II) | |
| | | | | | | -2.14 | 7.6 (III) | |

a) First row for each ion (I): $a = r_c + 2.76 \text{ Å}$ in eq. (9) and p_α from eq. (13). Second row (II): a and p_α according to [5] (see text). Third row (III): using p^e from eq. (14).

b) From [6].

c) From [7] for Cl, Br, I and [8] for OH.

d) From [9].

Table I (continued)

e) $\Sigma U = U(ep_\alpha) + U(p_\sigma p_\alpha) + U_{IND}$. $\Sigma U(I) = -1.21 + 0.06 + 0.60 (Cl^-)$;
 $-1.02 + 0.02 + 0.51 (Br^-)$; $-0.80 + 0.03 + 0.40 (I^-)$; $-1.26 + 0.04 + 0.63$
 (OH^-) . $\Sigma U(II) = -0.83 + 0.03 + 0.29 (Cl^-)$; $-0.68 + 0.02 + 0.23 (Br^-)$;
 $-0.55 + 0.02 + 0.19 (I^-)$; $-1.08 + 0.03 + 0.46 (OH^-)$. $N = 6$ for Cl^- ,
 Br^- , I^- and $N = 4$ for OH^- .

f) Calculated for $x = 0.08 \pm 0.06$ V for water [4].

Table 2

Ionization energies of clusters of water molecules

| $n^a)$ | $I_n^b)$ (eV) | $(12.62 - I_n)/(n - 1)$ (eV) |
|--------|------------------|---------------------------------|
| 1 | 12.62 | - |
| 3 | 11.93 | 0.35 |
| 4 | 11.55 | 0.36 |
| 5 | 11.31 | 0.33 |

a) Number of water molecules in cluster.

b) From SCF MO calculations in [2] except for $I_1 = 12.62$ eV (experimental).

I_n (11.88 eV) for $n = 2$ not used since it is obviously too low in comparison with I_n (11.93 eV) for $n = 3$.

Table 3

Reorganization free energy of the hydrated electron

| donor | E_t (eV) | E_{\max}^a (eV) | r_c (Å) | $R(D^-A)$ (eV) | R (eV) |
|-------------------------------|---------------|----------------------|--------------|-------------------|-------------|
| $\text{Fe}(\text{CN})_6^{4-}$ | 6.2 | 4.84 | 4.5 | 0.97 | 1.32 |
| SCN^- | 7.2 | 5.58 | 2.5 | 1.28 | 1.37 |
| $\text{S}_2\text{O}_3^{2-}$ | 7.3 | 5.76 | 3.5 | 1.10 | 1.27 |
| I^- | 7.4 | 5.48 | 2.16 | 1.36 | 1.15 |
| Br^- | 8.2 | 6.23 | 1.95 | 1.41 | 1.15 |
| OH^- | 8.6 | 6.63 | 1.47 | 1.54 | 1.28 |
| SO_4^{2-} | 8.7 | 7.08 | 2.3 | 1.33 | 1.42 |
| HPO_4^{2-} | 8.8 | 6.94 | 2.4 | 1.30 | 1.15 |
| Cl^- | 9.0 | 7.08 | 1.81 | 1.45 | 1.24 |
| $\text{H}_2\text{PO}_4^{2-}$ | 9.2 | 7.31 | 2.4 | 1.30 | 1.12 |

a) From [17].

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